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Austenitic Ni-Cr-Mo-Fe Alloy

Background of the Invention

The invention relates to an austenitic warm or cold-formable alloy.

Until now austenitic, austenitic-ferritic, ferritic as well as ferritic-martensitic steel on the one hand, and on the other hand nickel based alloys were used until now as materials for mechanical and at the same time chemically corrosion resistant components under heavy stress. The mechanical strength of austenitic steel is not sufficient for several applications. With ferritic-austenitic steel as well as with ferritic and ferritic-martensitic steel its poor processing behavior (hot forming, weldability) and the insufficient corrosion resistance are disadvantages.

EP-B1 0 334 410 has disclosed a nickel-chrome-molybdenum alloy that contains (by % of mass) the following alloy elements:

22.0 to 24.0 chrome
15.0 to 16.5 molybdenum
Up to 0.3 wolfram
Up to 1.5 iron
Up to 0.3 cobalt
Up to 0.1 silicon
Up to 0.5 manganese
up to 0.015 carbon
up to 0.4 vanadium
0.1 to 0.4 aluminum
0.001 to 0.4 magnesium
0.001 to 0.04 calcium

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The residue consists of nickel and includes and unavoidable impurities.

EP-B1 0 247 577 has disclosed an alloy on nickel basis containing chrome and molybdenum which can be hardened and containing, (in % by mass) the following alloy components:

Carbon max. 0.1
Manganese max. 5
Silicon max 1
Phosphor max 0.03
Sulfur max 0.03
Chrome 16-24
Molybdenum 7 to 12
Niobium 2 to 6
Titanium 0.50 to 2.5
Traces of aluminum up to 1
Boron max. 0.02
Zirconium max. 0.050
Cobalt max. 5
Copper max. 5

and containing in addition at least 50% nickel as residue as well as impurities due to production, with the total of chrome and molybdenum no greater than 31 and the total of niobium, titanium and aluminum is such that their total atomic weight percentage comes to 3.5 to 5 and combines in solution annealed and hardened form a 0.2% stretch limit of over 100 ksi (690 MN/m²) combined with a resistance to fissure corrosion and crevice

corrosion as well as against tension fissure corrosion in a chloride and sulfide environment at high temperature up to 260°C without requiring work below its recrystallization temperature.

If extreme corrosion conditions exist, it is necessary in many areas of application to have recourse to comparatively expensive Ni-Cr-Mo alloys with Fe contents limited in part to a maximum of 1%. But the alloys established on the market still are no longer sufficient to meet all requirements in today's chemical and petrochemical process technology, nor in the present environmental protection technology, in particular when at the same time high tensile limits or tensile strength are required. Problems often occur when known alloys are used as welding additives, in particular in the field of offshore technology, where mostly 6-Mo steel, duplex and super-duplex steel is welded.

Detailed Description of the Invention

It is the object of the present invention to propose an alloy that can be used in particular under extreme corrosive conditions and possesses at the same time extraordinarily high tensile limits and tensile strength. The alloy must possess high resistance to crevice and fissure corrosion as well as to removing corrosion and it must furthermore be possible to produce and process it without problems. For this reason the required strength of the alloy must already exist in the solution annealed or soft annealed state, so that additional hardening and heat treatment can be dispensed with.

This object is attained with an austenitic alloy which can be hot and cold-formed for use in aqueous, oxidizing media, consisting of the following alloy elements (in % by mass):

Cr	18.0-21.0
Fe	12.0-16.0
Mo	9.0-13.0
Co	max. 1.0
W	0.5-2.5
C	max. 0.025
N	0.05-0.25
Mn	max. 0.50
Si	max. 0.50
Ti	max. 0.02
Nb	0.05-0.5
Cu	max. 0.3
P	max. 0.010
Al	0.05-0.5
S	max. 0.005
Mg	0.005-0.030
Ca	0.001-0.01
V	max. 0.5
B	max. 0.005
Zr	0.001-0.030

The residue consists of nickel and includes impurities resulting from production.

An especially preferred alloy is composed of the following alloy elements (in % by mass):

Cr	19.0-20.0
Fe	13.0-15.0
Mo	10.0-12.0
Co	max. 1.0
W	1.0-2.0
C	max. 0.025
N	0.05-0.15
Mn	max. 0.50
Si	max. 0.50
Ti	max. 0.02
Nb	0.1-0.3

Cu	max. 0.3
P	max. 0.010
Al	0.10-0.35
S	max. 0.005
Mg	0.006-0.020
Ca	0.001-0.005
V	max. 0.30
B	max. 0.002
Zr	0.005-0.025

The residue consists of nickel and includes impurities resulting from production.

The total contents of aluminum + titanium are preferably limited to 0.30 (in % by mass). The same applies to the total contents of niobium + tantalate which are also kept at 0.30 (in % by mass).

Raising the iron content of the alloy according to the invention to 13 to 15 (in % by mass) results on the one hand in improved workability and formability, and on the other hand also to a considerable reduction of costs due to the lower metal price and the lowering of production costs. Contrary to generally held belief that less than 1% iron content is needed for build-up welding with Ni-Cr-Mo alloys on non-alloyed or low-alloyed steel, i.e. that a mixing up of iron in the welding deposit is prevented to a great extent, comparative investigations of the alloy A according to the invention and of the comparison alloy B which were used as welding additives for one- and two-layered build-up welding on St 52, shows that the iron content of the build-up welding carried out with the alloy A according to the invention is even lower than with the build-up welding with the comparison alloy B. This is shown in Fig. 1.

Elements	1-layered		2-layered	
	Alloy A	Alloy B	Alloy A	Alloy B
Ni	Residue	30	Residue	41.5
Cr	12.2	11	16.5	14.5
Mo	6.55	4.2	9.1	6
Fe	47.9	52.5	28.1	35
W	0.75	n.b.	1.13	n.b

Fig. 1: Chemical analyses of the build-up welding with the alloy A according to the invention and of the comparison alloy B on St 52.

The chemical composition (% by mass) of the comparison alloy B is as follows:

Cr 22
Fe 3.0
C 0.025
Mn 0.40
Si 0.40
Mo 8.0
Co 1.0
Al 0.40
Ti 0.40
Nb 3.5
P 0.010
S 0.010

Lowering the niobium content of the alloy A according to the invention to (in % by mass) preferably 0.1 to 0.3 results in far better weldability than with the comparison alloy B.

In addition a faultless and sediment-free, high-load bearing weld connection with duplex and super duplex steel having high nitrogen contents becomes at all possible.

Increasing the molybdenum content of the alloy A according to the invention to (in % by mass) 10 to 12, as well as increasing the W content to (in % by mass) 1 to 2 results in greater crevice and fissure corrosion resistance than alloy B, as is documented in Fig. 2.

Contrary to the instruction incorporated in EP-B1 0 247 577, according to which nitrogen contents up to 0.04% are acceptable and no precise specifications are given concerning the influence of nitrogen, the investigation of the influence of nitrogen in the alloy A according to the invention shows that nitrogen clearly increases the tensile limits and tensile strength on the one hand, and on the other hand clearly improves the corrosion resistance of the alloy A according to the invention. Fig. 3 shows this as an example of tensile strength R_m over nitrogen content, and Fig. 4 shows the tensile strength $R_{p0.2}$ over the nitrogen content for the alloy A according to the invention. The tensile limit is increased by approximately 30 % and the tensile strength by approximately 20 %.

The increase of the crevice corrosion resistance of the alloy according to the invention thanks to the addition of nitrogen is clearly shown in Fig. 5. In the state of the art, the crevice corrosion resistance is determined according to ASTM G48, method D, as well as "Green Death" solution (7% H_2SO_4 , 3% HCl , 1% $FeCl_3$, 1% $CuCl_2$). The critical crevice corrosion temperature increases in both tests as the content in nitrogen increases.

The alloy according to the present invention finds its application as an additive welding material in the offshore industry, in particular for connecting welding of long-seam welded pipes made of 6-Mo steel, duplex and super-duplex steel.

In addition, the possibility exists to utilize the alloy according to the invention as a welding additive material for build-up welding, in particular for flanges in the offshore field or for boiler pipes in waste burning plants.

Finally it is also possible to use the alloy according to the invention as a build-up welding band in plant construction and in addition to use it in gas channels of flue gas desulphuration installations.

In an extension of the invention, the alloy according to the invention can be obtained by melting scrap alloy combinations so that the narrow margins of the different alloy elements defined in the claims are implemented.